(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 October 2003 (30.10.2003)

PCT

(10) International Publication Number
WO 03/088740 A1

(51) International Patent Classification⁷: A01K 15/02, A23K 1/18, 1/00, C08J 5/04, C08K 5/053, C08L 3/00, B29C 67/24

(21) International Application Number: PCT/NL03/00292

(22) International Filing Date: 17 April 2003 (17.04.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02076595.4 19 April 2002 (19.04.2002) EP
60/373,775 19 April 2002 (19.04.2002) US

(71) Applicant (*for all designated States except US*): **COÖPERATIEVE VERKOOP- EN PRODUCTIEVERENIGING VAN AARDAPPELMEEL EN DERIVATEN AVEBE B.A.** [NL/NL]; Beneden Oosterdiep 27, NL-9641 JA Veendam (NL).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **PATER, Willem, Theodoor, Martinus** [NL/NL]; Kloosterlaan 21 A, NL-9675 JL Winschoten (NL). **VOLK, Richard** [NL/NL]; Kuifreiger 10, NL-9648 DR Wildervank (NL). **SCHENNINK, Geraldus, Gerardus, Johannes** [NL/NL]; Weversveld 57, NL-7031 CR Wehl (NL).

(74) Agent: **PRINS, A.W.**; Nieuwe Parklaan 97, NL-2587 BN Den Haag (NL).

(81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/088740 A1

(54) **Title:** PET'S CHEW AND MANUFACTURE PROCESS

(57) **Abstract:** The invention relates to a pet's chew prepared from natural materials of renewable sources. The chew is both edible and biodegradable, and furthermore has excellent mechanical properties giving it a long lasting time, even if used for strong animals such as large dogs.

Title: **PET'S CHEW AND MANUFACTURE PROCESS**

The invention relates to a process for producing a pet's chew and to a pet's chew obtainable by said process.

Chewable articles for pets such as dogs are well known in the art. These articles are of a flexible nature and serve as a toy for the pet as well as a means of keeping the pet's dentures in good condition. This type of article can be manufactured of different materials. Mainly, they can be divided in two classes: a non-edible variant and an edible variant.

The non-edible variant of a pet's chew can be made from synthetic plastic materials or from raw hide. They have good chewing qualities and, due to their mechanical properties, they have a fairly long lasting time. The greatest disadvantage of most of the non-edible chews is that they are hardly biodegradable, if at all.

Edible pet's chews are mostly produced from raw materials such as cereals, rice, milk and products derived therefrom such as casein, gelatin, and starches. Typically, they comprise numerous additives such as gums, meat or other products of animal origin, mineral oils or fats, vitamins, coloring agents, aromas or taste enhancers. The aim is, of course, to produce a coherent product having the desired mechanical properties to last a long time.

US patent 5,827,565 discloses a dog chew based on a thermoplastic starch, PARAGON IM 1010. This thermoplastic starch comprises a fairly large amount of calcium carbonate. The dog chew has a brittle character and is therefore less suitable for large dogs.

A disadvantage of most known edible chews is that their mechanical properties are not satisfactory. Due to the fact that they comprise a mixture of several ingredients, they are often brittle and often fall apart soon after a pet, such as a large dog, has set its teeth in it.

The present invention aims to provide a pet's chew prepared from natural materials of renewable sources, making the chew both edible and biodegradable. It is specifically desired that the chew has excellent mechanical

properties giving it a long lasting time, even if used for strong animals such as large dogs.

It has been found that an excellent pet's chew can be produced from thermoplastic starch by incorporating relatively large amounts of plasticizer and fibers. Accordingly, the invention relates to a process for preparing a pet's chew comprising

- preparing a mixture of a starch or a starch derivative, a plasticizer and a fibrous material;
- converting said mixture into a thermoplastic starch; and
- molding the thermoplastic starch into the desired pet's chew.

Due to the nature of the raw material on which a pet's chew according to the invention is based, starch, it is a biodegradable, edible product to which no risks associated with for instance BSE or Salmonella are associated. Furthermore, the specific composition of starting materials and the method of producing the chew makes that it has excellent mechanical properties. It is both tough and flexible, and has a long lasting time. It is a product which, in its mechanical properties, closely resembles known chews based on synthetic materials, while it is nevertheless edible and biodegradable. Due to its advantageous mechanical properties, a chew according to the invention has a beneficial effect on the dentures of a pet.

As mentioned, a pet's chew according to the invention is based on starch. In principle, the starch may be of any origin. Suitable examples are potato, wheat, corn, tapioca, rice and pea starches. It is preferred to use a wheat starch as this has been found to lead to a final product have a very good dimensional stability. The starch can be used in native form, but may also be physically or chemically modified. Of course, it is also possible to use combinations of native starch and modified starch, or combinations of different modified starches. Chemically modified starches which may be used are oxidized starches, carboxymethylated starches, hydroxyalkylated starches, acetylated starches, (partially) hydrolysed starches, and other derivatized

starches. An example of a suitable physically modified starch is a starch which has been subjected to ion exchange with, for instance, sodium or potassium ions.

The mixture that is to be converted into a thermoplastic starch according to the invention preferably comprises an amount of starch from 15 to 90 wt.%, preferably from 50 to 80 wt.%, based on dry solid weight of the mixture.

A preferred example of a modified starch is a starch hydrolysate. This is a native (or already otherwise modified) starch which has been subjected to a partial chemical or enzymatic hydrolysis. The extent of hydrolysis can be expressed in terms of the dextrose equivalent (DE). Starch which has not been subjected to hydrolysis has a DE of 0, whereas a completely hydrolysed starch has a DE of 100. In order to improve the flowing characteristics of a mixture from which a thermoplastic starch is prepared according to the invention, it is preferred to incorporate a starch hydrolysate having a DE up to 40, more preferably between 1 and 20. It has been found that the use of a partially modified starch in the preparation of a pet's chew according to the invention results in a product having superior characteristics. The mobility or viscosity of the mixture to be converted into a thermoplastic starch is increased, leading to an improved relaxation of the stress present in the material. As a result an increased dimensional stability in conjunction with an improved flexibility are achieved.

If desired, the starch may be mixed with other natural and biodegradable polymers such as cellulose and derivatives thereof, proteins such as zein or wheat proteins, or other polysaccharides such as gums (Arabic gum, guar gum and the like), pectin, or dragant. It is also possible to use a natural mixture of starch and proteins, such as flour, as a starting material.

In order to prepare a pet's chew of a starch material according to the invention, the starch is first converted into a thermoplastic starch. To that

end, a mixture of the starch with suitable additives is prepared, which mixture is then subjected to extrusion.

An important aspect of the invention is that the starch is mixed with a plasticizer. Although water also has plasticizing qualities in a process of producing a pet's chew according to the invention, an additional plasticizer is required. A preferred class of plasticizers is the class of polyols. This class comprises, amongst others, glycol, diethylene glycol, alkylene glycols, polyalkylene glycol, sorbitol, glycerol, glycerol mono-esters, and the like. Other suitable classes of plasticizers include esters of citric acid, and urea.

The amount of water that is preferably present in the starting mixture to prepare a pet's chew according to the invention from is from 7 to 35 wt.%, based on dry solid weight of the mixture. In addition to that, 5 to 30 wt.%, preferably 15 to 30 wt.%, and more preferably 18 to 30 wt.%, based on dry solid weight of the mixture, of the additional plasticizer is used. It has been found that these amounts of plasticizer lead to a very flexible product, while the dimensional stability of the final product, the pet's chew, is not endangered.

The mixture may further comprise other additives such as an emulsifier. Suitable examples of emulsifiers include lecithin and monoglycerides. An emulsifier will be preferably be present in an amount of from 0 to 5 wt.%, based on dry solid weight of the mixture.

Flow property enhancers/lubricants result in an increased processability (products with lower stress) of the thermoplastic starch. Examples of flow property enhancers are animal and vegetable oils and fats, especially hydrogenated oils and fats, and fatty acids and fatty acid derivatives such as mono- and diglycerides, fatty acid amides, metal salts and sorbitanesters of these fatty acids. Also fosfatides can be used as flow property enhancer. Ricinus oil and lecithin are examples of flow property enhancers/lubricants with a particular good performance. The amount of flow

property enhancer in the mixture to be converted to a thermoplastic starch can be up to 10%, more preferably between 0 and 5 wt.% based on dry solid weight.

Another important ingredient in the mixture is a fiber. Preferably, a pet food-grade fibrous material of natural origin is used. Preferred examples include cellulose, hemp, coconut, grass, flax, potato and other natural fibers. The fibers preferably have a length between 23 and 2000 μm, more preferably between 60 and 300 μm. The amount in which the fiber is preferably used is chosen in the range of from 1 to 35 wt.%, more preferably from 1 to 25 wt.%, and even more preferably 5 to 20 wt.%, based on the weight of dry solid mixture.

It is further possible to incorporate an organic or inorganic filler material, such as chalk or titanium oxide. A filler is preferably added in an amount of from 0 to 10 wt.%, based on the weight of dry solid mixture.

Other additives, such as pH regulators, health ingredients, coloring agents, enzymes, aromas or palatability enhancers can also be incorporated at this stage. For example, as pH regulator sodium bicarbonate or a phosphate buffer can be used. As health ingredients, vitamins or conjugated linolaic acid (CLA) can be used. As aroma or palatability enhancer, chicken, beef, or vegetable (e.g. mint or vanilla) aromas are often employed. As coloring agents, red, yellow, orange (iron oxide), green (chlorophyl) or white (titanium oxide) colorants are often employed. Typically, these additives will be added in an amount in the range of from 0 to 10 wt.%, based on dry solid weight of the mixture.

In order to prepare a thermoplastic starch of the above described mixture, it is subjected to an extrusion step. During the extrusion, the starch will be gelatinised. It is preferred to use a twin-type extruder operated at a temperature of from 95 to 180°C, more preferably from 100 to 150°C. As the mixture will undergo a thorough homogenisation during extrusion, it is not of crucial importance that all ingredients of the mixture are mixed so rigorously as to obtain a homogeneous mixture prior to extrusion. During the extrusion,

the starch will be converted from a ordered structure into an unordered, amorphous structure (destructurizing), which yields a thermoplastic, very well processable material.

In one embodiment, the pet's chew is molded in an extrusion step. In principle, it is possible that this is done in the same extrusion step as described above for obtaining the thermoplastic starch. However, it is preferred that a second extrusion step is performed. In that case, the second extrusion step is preferably carried out using a single-screw type extruder. Between the first and second extrusion steps, the thermoplastic material may be pressed through a mesh having a pore size of from 1 to 5 mm and cut to obtain a granulate material. This granulate material is preferably conditioned to an appropriate moisture content for the second extrusion step, which moisture content will generally be lower than that during the first extrusion step.

It is one of the advantages of the invention that the thermoplastic material that is formed in the extruder is sufficiently plastic in character to be pressed through a die. Under atmospheric conditions, the extruded product does not need to be foamed. The material that exits the extruder is either cut directly at the die opening to the desired size and shape, or is first cooled using forced air or nitrogen cooling and then cut to the desired size and shape. It is preferred that the material is not water cooled.

In another embodiment, the pet's chew is molded by injection molding. In accordance with this embodiment, it is preferred that the destructurized starch mixture is pressed through a mesh having a pore size of from 1 to 5 mm after extrusion, or preferably as a last step of the extrusion process. This will typically be done if the pet's chew is to be molded by injection molding. The obtained fibrous material is preferably cut to obtain a granulate material. This granulate material is preferably conditioned to a moisture content of from 5 to 20 wt.%, more preferably from 6 to 15 wt.%, even more preferably from 7 to 10 wt.%, based on the weight of the granulate material.

The moisture content can be controlled by using a vacuum zone in the extruder or by drying the granulate with hot air.

During injection molding, it is preferred to employ a processing temperature ranging from 80 to 200°C, more preferably from 110 to 170°C. If no, or not all additives like vitamins, coloring agents, aromas or taste enhancers have been added prior to extrusion, they can also be added to the thermoplastic starch granulate directly prior to injection molding.

The injection molding is preferably performed using a pressure in the barrel of the apparatus of below 1500 bar. The rate of injection is preferably kept relatively low and the injection channels are preferably relatively wide in order to keep the shear, that the material is exposed to, low.

Modification of the injection molding process may lead to an improved dimensional stability of the ultimate product. In order to achieve this, the process should be designed in such a way that the lowest amount of stresses is frozen in the matrix. This can be realised by increasing the processing temperature, low backpressure profiles and high mold temperatures, in combination with a low injection speed. As a result cycle times will increase. Therefore the use of a carrousel machine may be beneficial.

The mold into which the granulate material is injection molded, or the shape into which the material is cut after extrusion, preferably has the shape of a dog chew, such as the form of a bar, or a hollow or other natural shape, for instance mimicking the shape of a bone. Other shapes that are contemplated are of a marrow bone, pig's ear, tooth brush, or a combination of shapes such as a dog chew which is shaped like a bone on one side and like a tooth brush on the other. The final product is preferably packaged in a water, moisture and air proof packaging material.

It is to be noted that it is contemplated that the above described two embodiments of extrusion and injection molding can be combined, for instance by making use of a twin-screw extruder mounted on an injection molding

device. In accordance with such a combined embodiment, the extruded product is introduced into the injection molding chamber without intermediate production of granulate material.

The invention will now be further elucidated by the following, non-restrictive examples.

Example 1

120 parts by weight of food grade potato starch (moisture content 18%, obtained from AVEBE, Veendam, The Netherlands), X parts glycerol (for amounts, see table; type 1.26 wet, obtained from Chemproha), 3 parts by weight of lecithin (Topcitin 50 obtained from Lucas Meyer) and 27.5 parts by weight of cellulose fiber (type Arbocell BWW 40; average length of the fibre 200 μm; obtained from Rettenmaier) were mixed together. The amount of glycerol in the mixture was varied between 22.5 and 37.5 parts by weight.

The mixture was extruded in a Clextral BC 45 (L/D = 23) extruder. The temperature profile was: 20 (feeding zone) /115/120/115/85 (die) °C. The extrudate was granulated (pellet dimensions were about ø 4 mm) and dried to a moisture content of 9-10%. The granulate was injection moulded using an injection moulding apparatus Demag D60 NCIII-K, equipped with a standard PE-screw. Processing temperature was 150-160°C; the mould temperature was 20°C. Sample bars were moulded according to DIN 23167.

The sample bars were conditioned for 7 days at 20°C and 55 % relative humidity. For determination of mechanical properties, a Zwick Z 010 tensile tester with strain transducers was used. The shrinkage properties in the injection moulding direction were determined by comparing the length of the bars before and after conditioning.

An overview of the experiments and the results is presented in Table 1 (samples 1, 2 and 3). An increasing amount of glycerol leads to a decreasing stiffness, and thus to an increased flexibility, and an increasing shrinkage.

Example 2

120 parts by weight of food grade potato starch (moisture content 18%, obtained from AVEBE, Veendam, The Netherlands), 30 parts by weight of glycerol (type 1.26 wet, obtained from Chemproha), 3 parts by weight of lecithin (Topcitin 50 obtained from Lucas Meyer) and 28 parts by weight of cellulose fiber (type Arbocell obtained from Rettenmaier) were mixed together. The length of the cellulose fibers is varied between 23 and 2000 μm.

Using these mixtures, the procedure of Example 1 was repeated.

The results that were obtained are shown in Table 1 (see samples 4, 5, 6, and 7). It follows that an increasing fiber length has relatively little effect on the flexibility of the material. The dimensional stability increases significantly with increasing fiber length.

Example 3

120 parts by weight of food grade potato starch (moisture content 18%, obtained from AVEBE, Veendam, The Netherlands), 30 parts by weight of glycerol (type 1.26 wet, obtained from Chemproha), 3 parts by weight of lecithin (Topcitin 50 obtained from Lucas Meyer) and cellulose fiber (type Arbocell BWW 40 obtained from Rettenmaier) were mixed together. The amount of cellulose fiber was varied between 20 and 35 parts by weight.

Using these mixtures, the procedure of Example 1 was repeated.

The results are shown in Table 1 (see samples 1, 8, and 9). An increasing amount of fibers leads to an increasing stiffness, and thus to a reduced flexibility. It also leads to an increasing dimensional stability.

Example 4

100 parts by weight of dry, food grade starch, 30 parts by weight of glycerol (type 1.26 wet, obtained from Chemproha), 3 parts by weight of lecithin (Topcitin 50 obtained from Lucas Meyer) and 30 parts by dry solid weight of cellulose fiber (type Arbocell BWW 40 obtained from Rettenmaier)

were mixed together. In this experiment, two types of starch were compared. These were food grade potato starch (as employed in the previous examples) and food grade wheat starch (type Excelsior, AVEBE, Veendam, The Netherlands).

Using these mixtures, the procedure of Example 1 was repeated.

The results are shown in Table 1 (see samples 1 and 10). With both starches, a comparable stiffness was attained. However, the dimensional stability of the samples based on wheat starch was significantly better.

Example 5

116 parts by weight of food grade wheat starch (type Excelsior, moisture content 14%, obtained from Avebe, Veendam, The Netherlands), 33.2 parts by weight of glycerol (type 1.26 wet, obtained from Chemproha), 3 parts by weight of lecithin (Topcitin 50 obtained from Lucas Meyer) and 19 parts by dry solid weight of cellulose fiber (type Arbocell BWW 40 obtained from Rettenmaier) were mixed together. Except for the granulated extrudate, which was dried to a moisture content of 10-11%, the procedure of Example 1 was repeated using this mixture. The mechanical

The results are shown in Table 1 (see samples 11 and 12, respectively 2 and 5 weeks conditioned). It follows that the mechanical properities after 5 weeks conditioning are the same as after 2 weeks conditioning. Thus, the flexibility of the material is maintained for periods shorter than 6 weeks.

Table 1

Example	Sample #	Composition[1]	E-Modulus (Mpa)	Tensile strength (Mpa)	Strain at break (%)	Shrink-age (%)
I, III, IV	1	PN30G3L27.5BWW40	838 [31][2]	10.9 [0.3]	26.6 [1.9]	3.5
	2	PN22.5G3L27.5BWW40	1955 [46]	21.6 [0.1]	3.3 [0.2]	1.2
	3	PN37.5G3L27.5BWW40	106 [9]	5.0 [0.1]	46.4 [1.7]	8.2
II	4	PN30G3L28FIF400	1158 [52]	15. 5[0.5]	9.1 [1.5]	1.0
	5	PN30G3L28B400	1109 [43]	15.2 [0.4]	13.0 [2.3]	3.2
	6	PN30G3L28BWW40	1111 [48]	11.9 [0.2]	22.4 [2.1]	5.3
	7	PN30G3L28B600	1099 [53]	11.1 [0.1]	23.8 [1.6]	6.3
III	8	PN30G3L20BWW40	596 [61]	9.5 [0.1]	32.6 [2.8]	5.3
	9	PN30G3L35BWW40	1075 [51]	13.1 [0.2]	15.9 [2.6]	2.4
IV	10	WN30G3L27.5BWW40	720 [56]	10.9 [0.4]	20.6 [2.0]	2.4
V	11	WN33.2G3119BWW40 (2 weeks)	164 [30]	5.3 [0.1]	44.6 [4.1]	5.3
	12	WN33.2G3119BWW40 (5 weeks)	146 [5]	5.2 [0.1]	44.9 [1.7]	5.9

[1] The composition can be read as follows:

➢ starch:	PN:	potato starch
	WN:	wheat starch
➢ plasticizer:	G:	glycerol
➢ emulsifier:	L:	lecithin
➢ fiber:	BWW40:	Arbocel BWW40 200 µm fiber
	FIF400:	Arbocel FIF400 2000 µm fiber
	B400:	Arbocel B400 900 µm fiber
	B600:	Arbocel B600 60 µm fiber

[2] Standard deviation of the measurements is given in bracket

Claims

1. A process for preparing a pet's chew comprising

- preparing a mixture of a starch or a starch derivative, a plasticizer and a fibrous material;
- converting said mixture into a thermoplastic starch; and
- molding the thermoplastic starch into the desired pet's chew.

2. A process according to claim 1, wherein the starch is a potato, wheat, corn, tapioca, rice or pea starch.

3. A process according to claim 1 or 2, wherein the starch is a native starch or a chemically or physically modified starch.

4. A process according to any of the preceding claims, wherein the plasticizer is chosen from the group of polyols, esters of citric acid and urea.

5. A process according to claim 4, wherein the plasticizer is glycerol.

6. A process according to any of the preceding claims, wherein the plasticizer is present in the mixture in an amount of from 5 to 30 wt.%, preferably 18 to 30 wt.%, based on the weight of the mixture.

7. A process according to any of the preceding claims, wherein the fibrous material is chosen from the group of cellulose, hennep, coconut, grass, flax, potato and other natural fibers.

8. A process according to any of the preceding claims, wherein the fibrous material is present in the mixture in an amount of from 1 to 35 wt.%, preferably from 1 to 25, more preferably 5 to 20 wt.%, based on the weight of the mixture.

9. A process according to any of the preceding claims, wherein the fibrous material consists of fibers having a length between 23 and 2000 μm, preferably between 60 and 300 μm.

10. A process according to any of the preceding claims, wherein the mixture comprises water in an amount of from 7 to 35 wt.%, based on the weight of the mixture.

11. A process according to any of the preceding claims, wherein the starch derivative is a starch hydrolysate.

12. A process according to any of the preceding claims, wherein the mixture further comprises one or more additives chosen from the group of lecithin, monoglycerides, oils, fats (preferably rinicus oil), fatty acids or salts thereof (such as calcium stearate), filler materials, vitamins, coloring agents, aromas and taste enhancers.

13. A process according to any of the preceding claims, wherein the mixture is converted into a thermoplastic starch by extrusion at a temperature of from 95 to 180°C, preferably from 100 to 150°C.

14. A process according to claim 13, wherein the mixture is extruded through a mesh having a pore size of from 1 to 5 mm and cut to produce a granulate material.

15. A process according to any of the preceding claims wherein the moisture content of the thermoplastic starch is conditioned to 5 to 20 wt.%, preferably from 6 to 15 wt.%, more preferably from 7 to 10 wt.%, based on the weight of the thermoplastic starch.

16. A process according to any of the preceding claims, wherein the thermoplastic starch is molded by injection molding at a temperature ranging from 80 to 200°C, preferably from 110 to 170°C, into a mold of suitable shape and size.

17. A pet's chew obtainable by a process according to any of the preceding claims.

18. A pet's chew according to claim 17 having the form of a dog chew, bar or hollow or natural shape.

INTERNATIONAL SEARCH REPORT

Internati[redacted] -plication No
PCT/NL 03/00292

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01K15/02 A23K1/18 A23K1/00 C08J5/04 C08K5/053
C08L3/00 B29C67/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A01K A23K C08J C08K B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 552 897 A (COLGATE PALMOLIVE CO) 28 July 1993 (1993-07-28) claims 1-10; figure 1; example 1 ---	1-13,17, 18
X	WO 01 45517 A (NATURAL POLYMER INTERNAT CORP) 28 June 2001 (2001-06-28) page 7, line 30 -page 10, line 30; claims 1,6-9,13-18,26,37-42; table 1 ---	1-8, 11-13, 16-18
X	EP 0 838 153 A (TFH PUBLICATIONS INC) 29 April 1998 (1998-04-29) claims 18-24 ---	1,2,4,5, 10,15-18

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 June 2003	16/06/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Van Nieuwenhuize, O

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 08, 30 June 1999 (1999-06-30) & JP 11 056261 A (KIMURA KAZUTAKA), 2 March 1999 (1999-03-02) abstract ---	1,17
P,X	WO 02 067697 A (GAJRIA AJAY ;AXELROD GLEN (US); TFH PUBLICATIONS INC (US)) 6 September 2002 (2002-09-06) claims 1,25 ---	1-13,17, 18
Y	EP 1 018 519 A (TFH PUBLICATIONS INC) 12 July 2000 (2000-07-12) paragraph '0017!; claim 1 ---	14-16
Y	US 6 086 940 A (AXELROD GLEN S) 11 July 2000 (2000-07-11) claim 1 ---	14-16
A	WO 00 54578 A (LOMBI ROBERTO ;BASTIOLI CATIA (IT); NICOLINI MATTEO (IT); NOVAMONT) 21 September 2000 (2000-09-21) claims 1,3,4,6,7 ---	1-4
A	DE 198 30 775 A (BUNA SOW LEUNA OLEFINVERB GMBH) 13 January 2000 (2000-01-13) claim 7 ---	1
A	US 5 773 070 A (KAZEMZADEH MASSOUD) 30 June 1998 (1998-06-30) the whole document ---	1
A	US 5 419 283 A (LEO FRANCA) 30 May 1995 (1995-05-30) column 1, line 29 - line 51 -----	4,5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/NL 03/00292

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0552897	A	28-07-1993	US	5296209	A	22-03-1994
			AT	166537	T	15-06-1998
			AU	660755	B2	06-07-1995
			AU	3183393	A	22-07-1993
			CA	2086965	A1	18-07-1993
			DE	69318736	D1	02-07-1998
			DE	69318736	T2	26-11-1998
			DK	552897	T3	22-03-1999
			EP	0552897	A1	28-07-1993
			ES	2118183	T3	16-09-1998
			FI	930174	A	10-11-1993
			JP	5255055	A	05-10-1993
			NO	930149	A	19-07-1993
			PT	101177	A ,B	28-02-1994
			US	5407661	A	18-04-1995
WO 0145517	A	28-06-2001	US	6455083	B1	24-09-2002
			AU	7846500	A	03-07-2001
			CN	1413084	T	23-04-2003
			EP	1241946	A1	25-09-2002
			WO	0145517	A1	28-06-2001
EP 0838153	A	29-04-1998	US	5827565	A	27-10-1998
			US	5941197	A	24-08-1999
			US	6093427	A	25-07-2000
			AU	738391	B2	20-09-2001
			AU	4286997	A	30-04-1998
			CA	2219338	A1	25-04-1998
			EP	0838153	A1	29-04-1998
			US	6180161	B1	30-01-2001
			US	6110521	A	29-08-2000
			US	6126978	A	03-10-2000
			US	6200616	B1	13-03-2001
			US	6086940	A	11-07-2000
JP 11056261	A	02-03-1999	NONE			
WO 02067697	A	06-09-2002	US	2002119224	A1	29-08-2002
			WO	02067697	A1	06-09-2002
EP 1018519	A	12-07-2000	US	6159516	A	12-12-2000
			AU	6548699	A	13-07-2000
			CN	1263719	A	23-08-2000
			EP	1018519	A2	12-07-2000
			JP	2000201632	A	25-07-2000
			NZ	501716	A	27-04-2001
US 6086940	A	11-07-2000	US	5827565	A	27-10-1998
			US	6180161	B1	30-01-2001
			US	6110521	A	29-08-2000
			AU	738391	B2	20-09-2001
			AU	4286997	A	30-04-1998
			CA	2219338	A1	25-04-1998
			EP	0838153	A1	29-04-1998
			US	6126978	A	03-10-2000
			US	6200616	B1	13-03-2001
WO 0054578	A	21-09-2000	IT	TO990199	A1	15-09-2000

INTERNATIONAL SEARCH REPORT

Inf[redacted]ation on patent family members

Internati[redacted]Application No
PCT/NL 03/00292

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 0054578	A		AU	3166600	A	04-10-2000
			CA	2367153	A1	21-09-2000
			CZ	20013327	A3	13-03-2002
			WO	0054578	A1	21-09-2000
			EP	1164836	A1	02-01-2002
			HU	0200359	A2	29-05-2002
			JP	2002538793	T	19-11-2002
			NO	20014457	A	14-09-2001
DE 19830775	A	13-01-2000	DE	19830775	A1	13-01-2000
US 5773070	A	30-06-1998	AU	2442497	A	29-10-1997
			WO	9737826	A1	16-10-1997
US 5419283	A	30-05-1995	IT	226453	Z2	24-06-1997
			EP	0564764	A1	13-10-1993
			EP	0928558	A1	14-07-1999
			JP	5082260	U	09-11-1993